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WADC Technical Report 56-57

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(Title — UNCLASSIFIED)

A CADMIUM SULFIDE SOLAR ENERGY GENERATOR

David A. Hammond
Fred A. Shirland
The Harshaw Chemical Company

June 1956

WRIGHT AIR DEVELOPMENT CENTER   JUL 24 1956

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A CADMIUM SULFIDE SOLAR ENERGY GENERATOR

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June 1956

Aeronautical Research Laboratory
Contract AF 33(616)-2682
Project 1115
Task 70843

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

JUL 2 4 1956

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FOREWORD

This report was prepared by The Harshaw Chemical Company on work per-
formed as a project of Wright Air Development Center under Contract AF 33
(616)-2682, Task 70843, Project 1115, "Advanced Reconnaissance Systems."
It was initiated by the Physics Research Branch of Wright Air Development
Center with Dr. L. L. Antes as Task Scientist. This is the final report
of this contract.

The work on this task was performed by R. J. Baughman, M. Hacskaylo,
D. A. Hammond, E. D. Kennedy, W. A. Lasch, F. A. Shirland, and H. D.
Williams.

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ABSTRACT

Variously doped cadmium sulfide was grown in single crystal and polycrystalline form, contacted on one side with indium and a barrier electrode formed on the opposite face. The barrier electrode, while its exact nature is unknown, consisted of copper and cuprous oxide, which was processed to give a photovoltaic response. Such cells were used as solar energy converters. Energy conversion efficiencies up to 1% were obtained and batteries of cells were constructed which delivered about 100 milliwatts when illuminated with light equivalent to sunlight outside the earth's atmosphere.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Aldro Lingard

ALDRO LINGARD, Colonel, USAF
Chief, Aeronautical Research Laboratory
Directorate of Research

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INTRODUCTION

Preliminary work at WADC[1] indicated the possibility that cadmium sulfide would be a more desirable solar energy converter material in some important respects than other known semi-conducting materials. In particular, CdS would convert light to electrical energy at temperatures well above the point where such materials as germanium and silicon would cease to operate. The purpose of this contract was to develop further the WADC techniques for making CdS solar energy converters and to manufacture a battery of such cells capable of delivering, if possible, up to 5 watts of power.

The WADC method[2] consisted of growing single crystals by the sublimation of Fisher Pure Grade CdS in an H_2S atmosphere in a fused quartz tube. A solid crystal so grown was prepared by grinding two parallel surfaces to serve as electrode faces. One side was electroplated with indium for a collector electrode. The other side was electroplated in a $CuSO_4$ solution and heated to form a barrier electrode. When illuminated, the cell so formed developed a voltage between the two electrodes.

Crystal growth work at Harshaw was directed towards securing larger sized single crystals in quantity. Consistent growth could not be obtained using an impure CdS, and a program of controlled impurity additions to pure CdS was carried out. The use of larger furnaces and other methods of growth were also tried. Making batteries from the best single crystals obtainable was a slow, painstaking and expensive operation.

Hence, the effort was shifted to polycrystalline plate growth, and large pieces were obtained.

The conversion efficiency obtained from polycrystalline plates was the same as obtained from single crystals, but did not exceed 1%. In an effort to obtain higher efficiencies, much work was done to improve the techniques of forming the barrier. This included electroplating various materials under different conditions and vacuum deposition of several materials. Comparable efficiencies were observed from some of these methods, but no overall improvement was secured.

A line of attack was then followed to determine the nature of the barrier. Several types of diffused barriers were evaluated. Barriers were formed under different heating and atmospheric conditions. While considerable information regarding the nature of the barrier was gathered, a more complete understanding is necessary before greatly improved efficiencies can be reached.

RAW MATERIAL

Fisher CdS, as used at WADC, was not immediately available so Harshaw-produced CdS, made from Mallinckrodt's Analytical Reagent Grade $Cd(NO_3)_2$, was used for the first few runs. The undoped crystals grown from this CdS were very high in resistance. Then a sample of an Experimental Grade of the New Jersey Zinc Company was tried. Crystals from this CdS were dark in color and varied widely in resistance. Some photovoltaic output was obtained from one run of these crystals.

Somewhat better results were secured with undoped Fisher's Pure Grade CdS. A number of runs were made using this material, but crystal growth was extremely variable. The impurity content of the Fisher CdS

was high and varied from lot to lot, hence General Electric Company's Luminescent Grade CdS was tried, with the impurities being added in controlled amounts. The GE CdS was as pure as any known commercially available material. More consistent results were obtained with it and this CdS was used for most of the subsequent runs.

Toward the end of the contract period work was started to secure a "super pure" material. General Electric Company's Chemical Division had been requested to make such a material. However, after several attempts they gave up, so an effort to produce it was made at Harshaw. Two batches of "super pure" CdS were produced by the vapor phase reaction of the purified elements. Insufficient time was available for the completion of this work, but an improvement in purity was gained. It is believed that this method can be used to produce a still higher purity CdS.

Representative spectrographic analyses of these various source materials are given in Table 1. Since the amount of impurities approach the limits of spectrographic analysis, it is questionable whether some of the elements detected are actually in the CdS or are a part of the "high purity" carbon electrodes used for the test.

DOPING

Due to considerable variation in the impurity concentration of the Fisher "Pure" CdS used initially, it was found desirable to start with a purer base material and add the required impurity in closely controlled amounts. General Electric Company's luminescent grade CdS was chosen as the best base material for this work.

TABLE 1.

RAW MATERIAL SPECTROGRAPHIC ANALYSES OF CdS

Samples of

1. Fisher Pure Grade

2. Sample New Jersey Zinc, Experimental Grade

3. General Electric Luminescent Grade

4. Harshaw "Lot 1"

5. Harshaw "Super Pure"

Approximate Values

VS – Very Strong Over 5%
S   – Strong   1–5 %
M   – Moderate   .1–1 %
W   – Weak   .01–.1%
T   – Trace   .001–.01%
FT – Faint Trace
VFT – Very Faint Trace

—— Not Detected

Blank– Not Specifically Checked

	1	2	3	4	5		1	2	3	4	5
Aluminum	FT	FT	VFT	VFT	VFT	Molybdenum	--	--	--	--	--
Antimony	VFT	--	--	--	--	Nickel	VFT	--	--	--	--
Arsenic	T	--	--	--	--	Platinum	--	--	--	--	--
Barium	--	--	--	--	--	Potassium					
Beryllium	--	--	--	--	--	Scandium					
Bismuth	--	--	--	--	--	Silicon	T	M	--	T	--
Boron						Silver	--	VFT	--	VFT	--
Cadmium	VS	VS	VS	VS	VS	Sodium	--	--	--	--	--
Cesium						Strontium					
Calcium	W	T	--	--	--	Tantalum					
Cerium						Thallium	T	--	--	--	--
Chromium	--	--	--	--	--	Thorium					
Cobalt	--	--	--	--	--	Tin	--	--	--	--	--
Columbium						Titanium	--	T	--	--	--
Copper	VFT	VFT	VFT	VFT	VFT	Tungsten					
Gallium						Uranium					
Germanium	--	--	--	--	--	Vanadium	--	--	--	--	--
Gold						Zinc	M	M	T	--	--
Indium	W	T	--	--	--	Zirconium					
Iron	W	T	VFT	VFT	VFT						
Lanthanum											
Lead	T	FT	T	FT	VFT						
Lithium											
Magnesium	W	T	VFT	VFT	VFT						
Manganese	VFT	VFT	--	--	--						
Mercury											

In doping there are at least two factors to be considered: the effect on crystal growth and the effect on photovoltaic output. Since zinc and indium were the main impurities in all the early runs which produced crystals of reasonable electrical resistance and photovoltaic power, various combinations of zinc and indium doping were tried. At first zinc (in the form of ZnS) appeared to help crystal growth but did not contribute to the photovoltaic effect. Later, satisfactory growth was secured without zinc additions, and work was centered on indium doping.

Single crystals have been grown from CdS with In_2S_3 added in the proportions of 0.4, 0.2, 0.1, 0.05, 0.033, 0.02 and 0.01% by weight. The growth characteristics of crystals doped with 0.1% or more In_2S_3 were progressively more striated and hollow as the indium concentration was decreased. Pure CdS growth runs gave mostly hollow or small needle-shaped crystals. However, the lower concentrations of indium appeared to give better photovoltaic output, and most subsequent single crystal growth runs were made using 0.05% In_2S_3. This evaluation was greatly complicated by the lack of a good reproducible method of barrier formation.

The incorporation of halides[3], chloride in particular, in CdS is another method of lowering its electrical resistance. To investigate the photovoltaic effect of halogen-doped CdS, a run doped with 0.05% In_2S_3 plus 0.05% $CdCl_2$ gave crystals that were essentially the same as those run with 0.05% In_2S_3 alone. Another run with 0.10% $CdCl_2$ only as the dope yielded small crystals, but a few of these that were processed gave fair-to-good photovoltaic power.

One run with 0.01% In_2S_3 plus 0.05% NaCl was followed by two runs with 0.05% In_2S_3 plus 0.05% NaCl. The first produced only small unusable crystals. The second yielded fair sized crystals with output about the same as crystals with 0.05% In_2S_3 only as the dope. The third run gave crystals with such high resistance they could not be electroplated. Since all of these NaCl mixtures attacked the quartz tubes severely, no additional NaCl runs were made.

$In_2(SO_4)_3$, Ag_2S, CuS, CdO, and Cd (metal) were also tried as doping materials. None of these showed any advantage. $In_2(SO_4)_3$ gave small but solid crystals. Cadmium metal used as a dope produced very small black crystals. The cadmium metal reacted with the H_2S, so it was not known how much excess cadmium was available for the crystals. One run of pure material in an H_2 atmosphere gave only clusters of small needles near the ends of the tube. There was similar needle growth from the cadmium metal doped run.

Polycrystalline plates could be grown equally well regardless of the type or amounts of impurities present in the cadmium sulfide. The presence of impurities changed the conditions of temperature and time but, since the growth could be visually observed, these changes in conditions could be readily made.

CRYSTAL GROWTH

Single crystals of CdS were grown by the Reynolds & Czyzak method[4] of sublimation and crystallization. Furnaces were of WADC design, with subsequent modifications. Three furnaces were built for a 2 inch ID tube, one for a 3-1/2 inch tube, and one for an 8 inch tube. Figure 1 illustrates

FIGURE 1

HORIZONTAL GROWTH APPARATUS
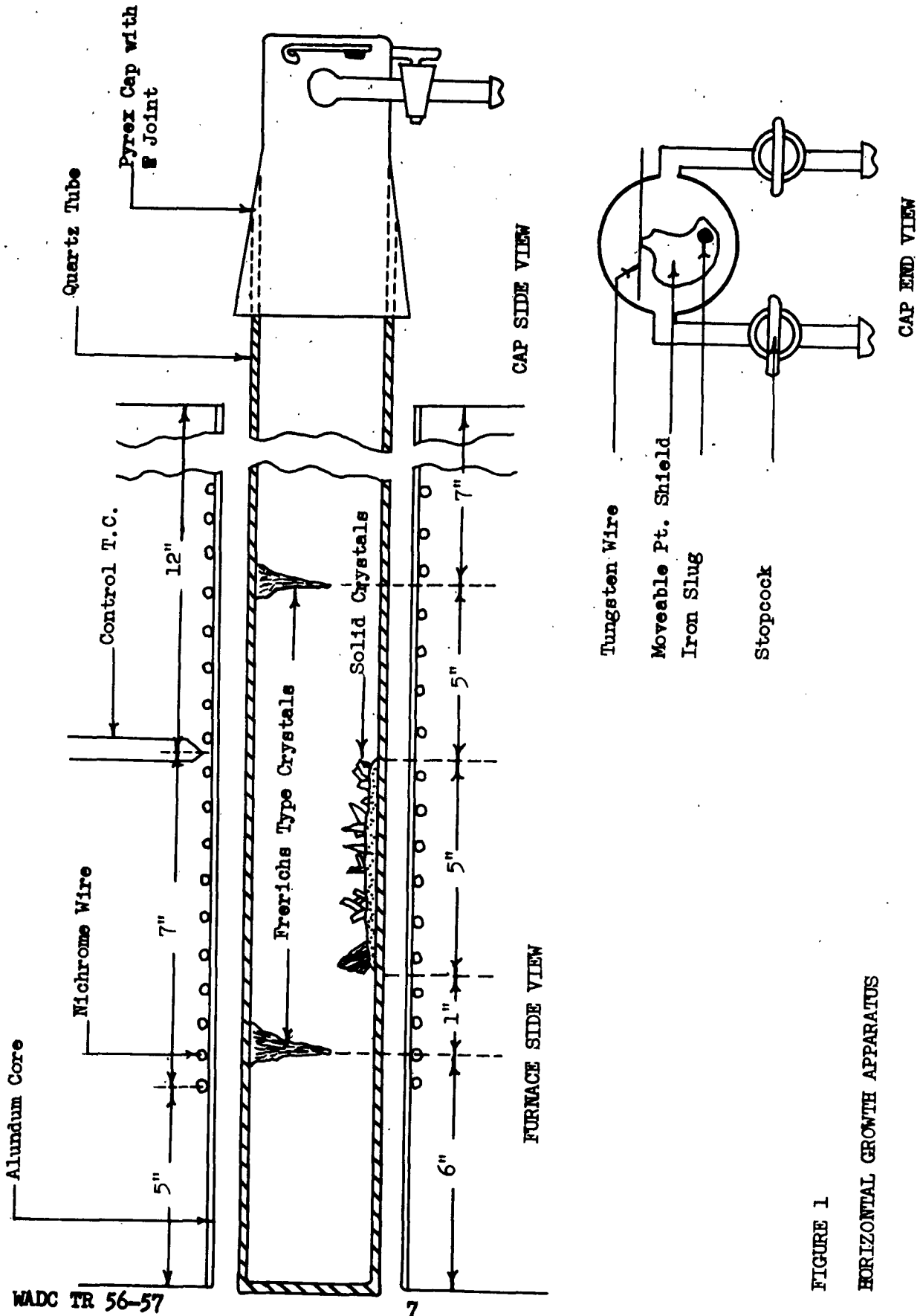
CAP SIDE VIEW

CAP END VIEW

FURNACE SIDE VIEW

Pyrex Cap with F Joint

Quartz Tube

Control T.C.

Nichrome Wire

Alundum Core

Frerichs Type Crystals

Solid Crystals

Tungsten Wire

Moveable Pt. Shield

Iron Slug

Stopcock

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the furnace construction, the position of the charge, and the locations of crystal growth. Both on-off and proportioning-type temperature controllers were used and found to be equally satisfactory.

A typical run in a 2 inch furnace was carried out in the following manner. The desired impurity addition was stirred into 150 gms of dried CdS powder and placed in the quartz tube in the furnace which had been pre-heated to 200°C. A safety manometer was connected to one outlet, and the tube evacuated to less than 1 mm pressure and then filled with H_2S at atmospheric pressure. Purging was repeated 3 times in this manner, and the tube was finally filled with H_2S at 200 mm pressure and sealed off. The temperature was increased to the operating point (approx. 1025 to 1050°C, depending on the material) in about 24 hours. The H_2S pressure inside the tube rose to atmospheric pressure at the operating temperature, with any excess H_2S flowing out through the safety manometer. This feature is important since the sublimation temperature of CdS changes with pressure. The furnace was held at the operating temperature for 5 to 6 days. Growth was observed through the window at the end of the tube and adjustments in temperature made as indicated. When the crystal growth had apparently reached its maximum the temperature was programmed down to 500°C in about 6 hours. The furnace was turned off and allowed to cool to 200°C. The tube was removed from the furnace, opened and unloaded.

It appeared that moisture in the raw material was causing difficulty by producing hollow crystals and possibly forming CdO (thus changing the crystal composition). Consequently, a standard drying procedure was adopted. This consisted of purging a muffle furnace loaded with the CdS

powder by a nitrogen sweep to remove oxygen, heating to 300°C for 18 hours, and then to 450°C for 4 hours. This material was then cooled to 200°C. The nitrogen sweep was maintained throughout. The dried CdS was then unloaded and stored in an oven at 150°C until used.

Most of the growth runs were made using 2 inch fused quartz tubes. Occasionally, very much more promising results were obtained with the 3-1/2 inch tube. In a few cases more than 100 CdS single crystals of useable size were obtained in a single run of this tube. Some work was done with an 8 inch ID fused quartz tube. While a few good crystals were obtained, a number of difficulties were encountered with the operation of such a large furnace. Chiefly, burnouts of the Nichrome winding occurred. The amount of work indicated here precluded further evaluation of the 8 inch diameter tube during the period of the present contract.

A high temperature porcelain tube was tried in place of the 3-1/2 inch fused quartz tube, but the crystals from it were very dark. Apparently some impurity fired out of the porcelain, so fused quartz tubes only were used thereafter.

Since the best formed crystals were found in the hottest part of the tube, one 2 inch furnace was wound with a gradient winding so that the position of the hottest portion of the tube could be better controlled with respect to the position of the charged material. This gave an improvement in growth, hence another 2 inch furnace was converted to a gradient winding, and the 8 inch furnace was built with such a winding.

Platinum baffles were tried in various positions in an effort to control the strong thermal currents encountered in the tubes. These thermal currents were much more severe in the large diameter tubes. If the baffles

were placed too far into the hot zone they acted as a base for poly-
crystalline plate growth. These baffles were attacked badly by H_2S
at high temperatures.

The largest usable crystals grown by the method of sublimation
and crystallization were about 20 mm long by 6 mm wide by 6 mm thick at
the base. Very few of this size were obtained. Most of the crystals
were too small to economically cut them to a standard shape so that they
could conveniently be prepared for assembly into large-area solar
batteries. Hence, other methods of crystal growth were evaluated, includ-
ing growth on a seed crystal and growth from a fused salt melt.

No promising results were secured by placing seed crystals in the
sublimation and crystallization furnaces. Seed crystals were tried in
these furnaces on the end of quartz rods, in various spots in and near
the pile of charged CdS powder, and wedged into a hole in a quartz baffle
plate placed in various sites in the furnace tube. In some cases the seed
sublimed away and in other cases clusters of small crystals grew from the
seed crystal with no particular orientation. Control of temperature
gradient in the growth zone and seed temperature were believed to be
important, but were very difficult to achieve.

A Bishop and Liebson tube[5] was constructed in an attempt to grow
on a CdS seed crystal by the vapor reaction method. In order to determine
the growth characteristics of this furnace at different temperature condi-
tions, several preliminary runs were made without seed crystals. Cadmium
metal was vaporized and carried into one arm of the tube with a helium
sweep. H_2S vapor was fed through the second arm. In some cases needle-
like CdS crystals were obtained in the outlet arm and, in one instance,

very small plate-like crystals were obtained. When seed crystals were mounted to quartz rods and held in various positions in the main chamber no oriented growth on the seeds was obtained.

In attempting to grow single crystals from molten salts (with CdS in solution) the ingredients were mixed in platinum crucibles, heated over a Fisher burner until molten, held for a few minutes, and then cooled until solid. The solidified mass was broken open and examined microscopically. The mixtures listed in Table 2 were tried. Mixtures Nos. 2, 4 and 10 showed evidence of the CdS going into solution and crystallizing on cooling. These mixtures were re-run in a small tube furnace in open containers with a controlled cooling cycle. Mixture No. 2 produced some small thin plates of CdS on an early run when the furnace burned out. Many re-runs were tried with varying furnace conditions, but no larger crystals were obtained. Mixtures No. 4 and No. 10, when re-run in the tube furnace, gave no crystals at all. In these the K_2S_x, which was apparently the solvent for CdS, was decomposed by the longer period at high temperature.

There was not sufficient time available to completely evaluate these other methods of crystal growth. However, sufficient experience was gained to permit efficient planning of further investigations of these methods at a later time.

Early in the contract, during the work with platinum baffles, it was found that when a baffle was placed near the hottest section of the tube, a polycrystalline CdS growth was obtained on the surface of the baffle. This growth usually covered the baffle to a depth of 1 or 2 mm or more, and the individual crystal grains were as much as several millimeters across and aligned so that their optical axes were perpendicular to the face of the baffle.

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TABLE 2.

<u>MIXTURES FOR MELT GROWTH</u>

<u>Run</u>	<u>Ingredients</u>	<u>Proportions</u>
1	KF, CdS	5:2
2	KF, CdS	4:1
3	KF, BaS, CdS	5:5:1
4	KF, K_2S_x, CdS	5:5:1
5	KHF_2, CdS	5:1
6	KHF_2, BaS, CdS	5:5:1
7	KHF_2, K_2S_x, CdS	5:5:1
8	NaCl, K_2S_x, CdS	5:5:1
9	K_2CO_3, K_2S_x, CdS	5:5:1
10	K_2SO_3, S, CdS	5:5:1
11	KF, S, CdS	5:5:1
12	KHF_2, S, CdS	5:5:1
13	KHF_2, KCl, CdS	5:5:1
14	Li_2CO_3, K_2S_x, CdS	5:5:1
15	$Cd(NO_3)_2$, CdS	10:1
16	$Cd(NO_3)_2$, K_2S_x, CdS	10:10:1

Some sections of these polycrystalline growths as large as 3 to 4 sq cm in area were broken off of these baffles and a few were successfully processed into solar cells. This processing was difficult because, in breaking off large pieces, cracks frequently opened up along the boundaries between individual crystal grains. These cracks made it difficult to hold the large sections together and caused trouble by shorting out the electrodes during the later electroplating operations. When other methods failed to produce large single crystals of CdS, this method of growing large polycrystalline plates was investigated more extensively. The difficulty with platinum baffles being attacked by H_2S was avoided by using quartz plates for baffles. The trouble with cracked CdS polycrystalline growths was circumvented by polishing the surface of the quartz baffle. When the surfaces of these plates were ground flat and given an optical polish, the CdS polycrystalline plate growth could be slid off of the baffle in one piece with very little danger of cracking.

Cadmium sulfide plates formed in horizontal furnaces were always thicker at the bottom edge than at the top. To get a more uniform thickness the furnaces were operated in a vertical position. Figure 2 illustrates this construction. Polycrystalline cadmium sulfide plates were grown readily to a thickness of 2 to 7 mm and were made up of irregularly shaped grains which varied in size from 1 to 5 mm across. Figure 3 shows the largest such growth obtained, which measured 90 mm long by 40 mm in diameter, and weighed 399 gms, though it appeared to be partially hollow. In order to form these polycrystalline plates it was necessary to place the quartz discs in the furnace so that they were above 1000°C but at a lower temperature than the CdS charge material. Higher temperatures than
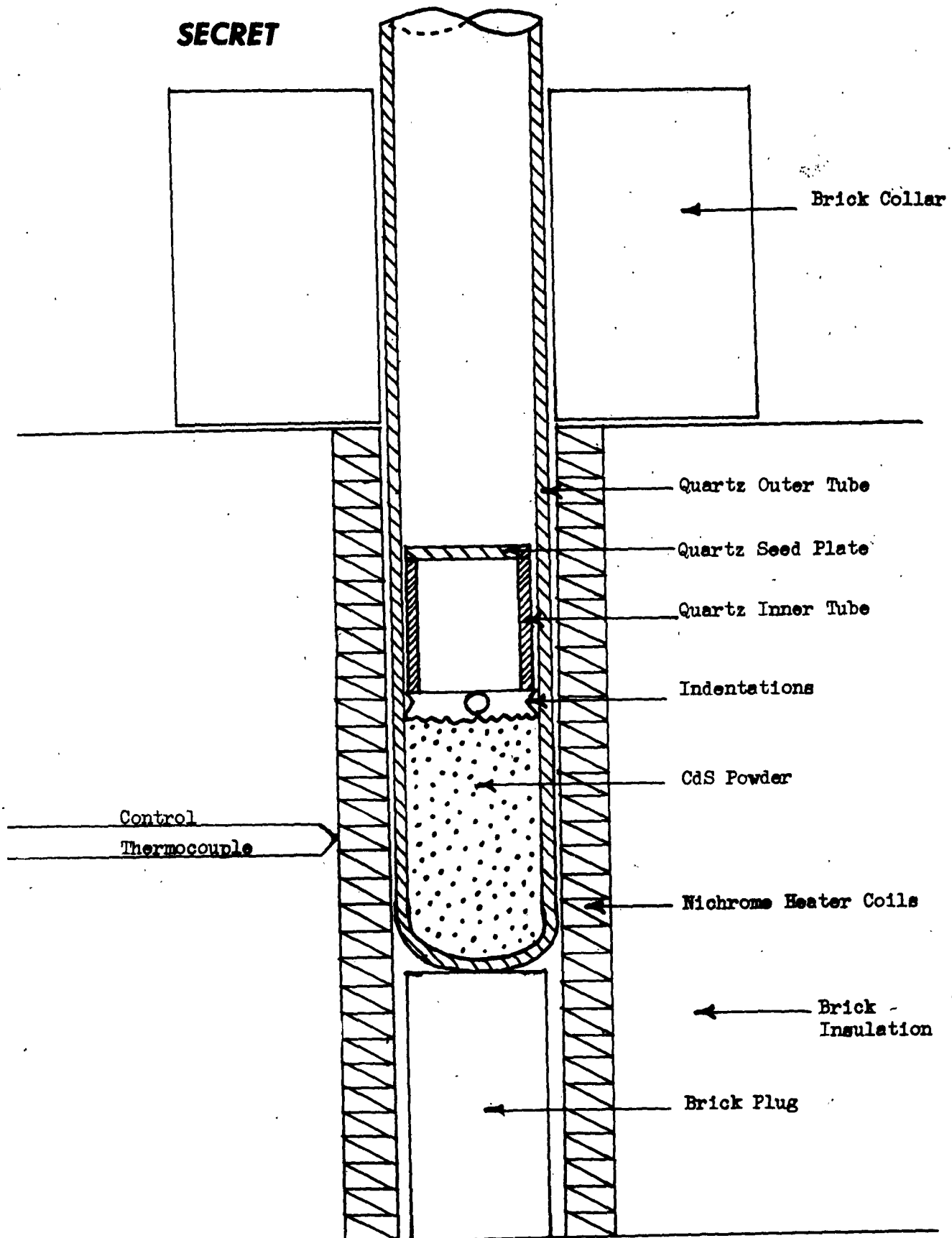
Figure 2. Vertical Growth Apparatus

Figure 3.

Large Polycrystalline Growth

these seemed to give larger grains and clearer plates. However, operating at the higher temperatures was impractical because of constant furnace burn-outs and disintegration of the fused quartz tubes, which were difficult to replace.

Polycrystalline plates, as used in Batteries B-3 to B-8 inclusive, were grown in 1 inch vertical tube furnaces. Four such furnaces were built, as well as three 2 inch vertical furnaces. (One of the 2 inch furnaces used four "Globar" silicon carbide heating elements in place of the Nichrome coils.) The procedure for these runs was speeded up over that for the single crystal growth runs. After charging and purging, the temperature was raised to about 1150°C in approx. 15 minutes and held there for 4 hours. The power was then cut off, the tube allowed to cool to 400°C and removed from the furnace. It was unloaded as soon as it could be handled. The entire cycle took about 6 hours, hence it was possible to make as many as 4 plates per day in each such furnace. A plate 4 mm thick by 20 mm in diameter, weighing approx. 8 gms, resulted from a 10 gm material charge.

During the contract period 120 single crystal furnace runs and 322 polycrystalline plate growth runs were made. All but 2 of the single crystal runs were in horizontal furnaces, and all but 16 of the plate runs were in vertical furnaces.

CRYSTAL PREPARATION FOR ELECTRODING

Most of the single crystals available were small and odd shaped. It was found desirable to embed them in plastic, as this made it much easier to bring them down to thickness, and helped prevent shorting out of the crystals during subsequent plating of the electrodes. Different

resins tried for this purpose included: epoxy, polystyrene, vinyl monomer, acrylic, and allyl diglycol carbonate. Epoxy resin was found most satisfactory because of the convenience in casting, low shrinkage, and workability when cured. The particular epoxy resin used was Ciba Company's "Araldite" No. 502 Resin with Hardener HN-951. This resin is light amber in color and will withstand a temperature of 120°C without appreciable discoloration.

Crystals were prepared for electroding by potting them in resin, slicing them on a diamond saw to the approximate thickness desired, and grinding and polishing them to an optical finish with successive grits of alumina. There has been some doubt as to the necessity for an optical finish. Several experiments to evaluate this were inconclusive. In some cases, at least, equivalent results were obtained by eliminating the polishing entirely.

In order to minimize the possible deleterious effects of unknown and varying contaminants on the crystal surface, an evaluation of cleaning and etching of the crystal prior to electroding was undertaken. Various cleaning methods were tried, including scrubbing with a hot solution of tri-sodium phosphate, treating with a strong (30%) solution of H_2O_2, and rinsing in distilled water. It seemed that mere water rinsing and rubbing with clean paper tissue was just as satisfactory. On the other hand, etching prior to electroding did appear to give higher crystal outputs, on the average, and more uniform results. A number of etchants were tested including: HNO_3, HCl, NH_4OH, NH_4NO_3, $(NH_4)_2S_x$, H_3PO_4, HF, CH_3COOH, and $NaCN$. Some of these did not appear to etch cadmium sulfide, and some which did left a sulfur film residue on the crystal which was difficult to remove. Either concentrated H_3PO_4 or 1:1 HCl etched well, and crystals so etched performed

satisfactorily if they were rinsed thoroughly prior to plating.

These strong etchants worked rapidly and it was difficult to control closely the amount of crystal removed. Better results were obtained using lower acid concentrations and etching electrolytically. A solution of 1 to 2% HCl with about 0.5% "Tergitol 4" Surface Active Agent added was finally used. The crystal was made anodic and only sufficient voltage (in the range of 10 to 15 volts) to produce a very slow release of gas bubbles from a platinum cathode was used. The etching action was carried on for about 2 to 5 minutes, sufficient to remove a definite layer from the surface of the crystal. Allowing the etching to proceed too rapidly, or for too long a period, resulted in an undercutting of the crystal surface. After etching, the crystals were rinsed several times in distilled water.

Several attempts were made to evaluate the effect of crystal thickness. One experiment gave the results as plotted in Figure 4. A medium sized crystal was cut so that its cross sectional area was nearly constant over its length. This crystal was potted in an opaque epoxy resin and the ends ground and polished. A barrier was established on one end and this barrier was contacted with silver print and a copper wire lead. The whole assembly was then re-potted in epoxy resin so that the barrier electrode was completely protected by resin. Before and after re-potting, the length (i.e., thickness) was carefully measured. On the opposite end of the crystal an indium electrode was evaporated and overlaid with silver print. The output of the cell was measured under various resistive loads. The crystal was then reduced in thickness (by grinding away the indium-electroded end), re-polished, and the indium electrode re-applied. The

Power Output - MW/CM²

Crystal Thickness - Millimeters

Open Circuit Voltage - Volts
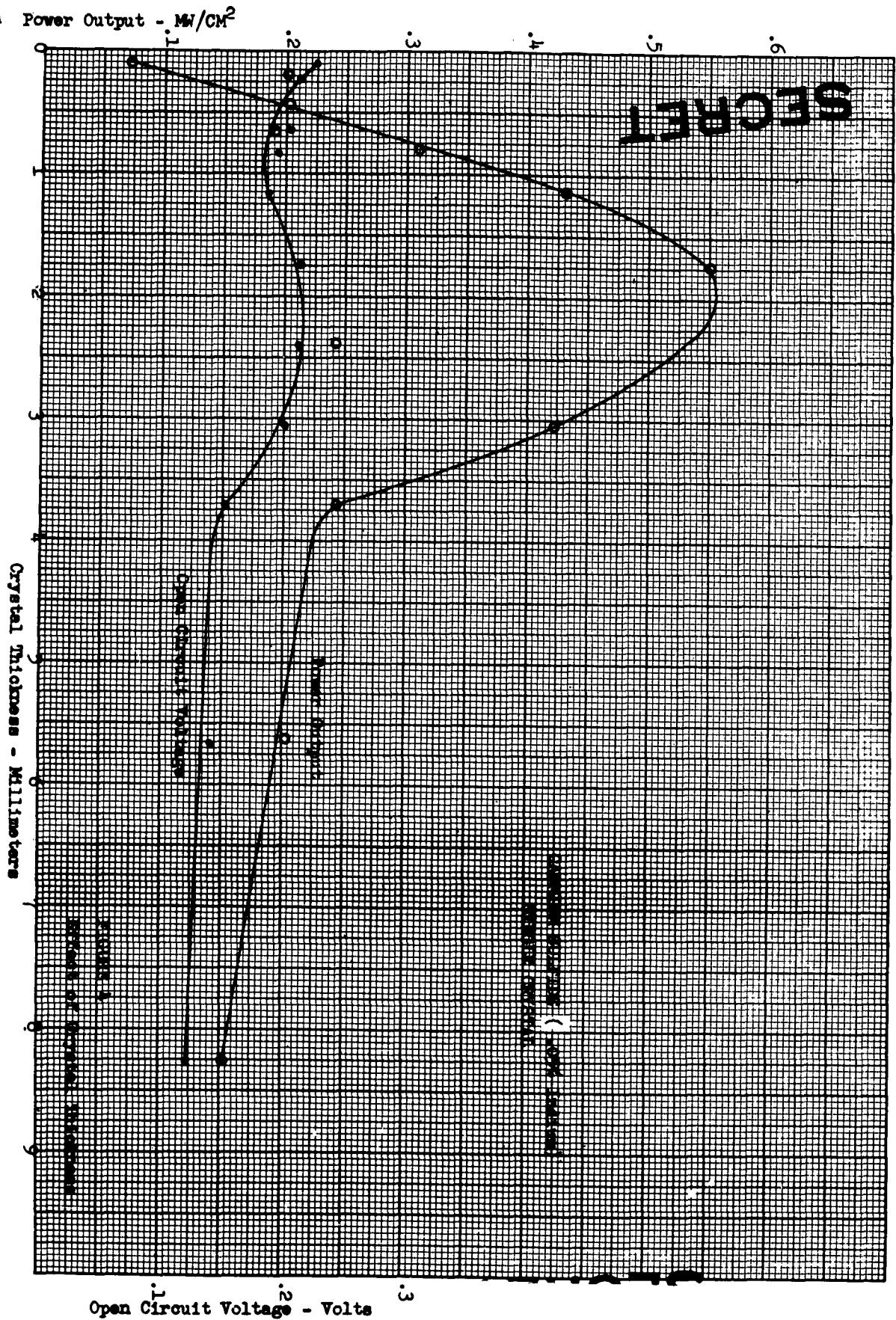
crystal output was re-measured, and the whole process repeated in steps until the thickness was only 0.002 in. At this point it cracked and broke into several pieces. It is seen from Figure 4 that while several points are out of line a smooth curve can be plotted and that the power output appears to have a fairly sharp maximum at about 2 mm thickness. The open circuit voltage rose as the thickness decreased, fell off slightly just below 2 mm, but then rose again slightly as the crystal approached zero thickness. A second crystal run in the same manner gave similar results down to just under 2 mm, but became very erratic below this value. Several re-runs were attempted but were unsuccessful due to breakage of the crystals in processing.

COLLECTOR ELECTRODE

In general, the collector electrode has consisted of an electro-plated indium stripe across one face of the crystal overlaid with a silver conductive paint. General Cement Company's "Silver Print" No. 21-2 was used. Initially, the indium electrode was plated from a solution of $InCl_3$ (or $In_2(SO_4)_3$) and NaCN. However, repeated difficulty with poor indium electrode adhesion prompted further work on this plating process. It was observed in plating indium from the cyanide bath that an etching of the crystal occurred under the plated electrode. When the NaCN was eliminated and the solution adjusted with HCl to about pH 1, an excellent, closely-adhering electrode resulted. Occasional difficulties with poorly adhering indium electrodes from this bath are attributable to inadequately-cleaned crystals.

Gallium was tried as a collector electrode material but was not very promising because of its very low melting point. Also, some difficulty with its wetting CdS was experienced.

In the work with electrolytic etching it was observed that when the crystal was made cathodic instead of anodic, some etching took place, and at the same time a cadmium electrode was formed on the crystal. This cadmium electrode was very closely adhering and excellent in appearance. Also, it gave a very good ohmic contact to the crystal. It was found that this deposit could be formed using different electrolytes, but weak HCl seemed most satisfactory. Further evaluation of this cadmium electrode disclosed that the acid concentration and current density were important to securing an adherent electrode. Since cadmium seemed to have no particular advantage over indium as a collector electrode material, no further work was done on this method.

Silver Print has been used to overlay the collector electrode in order to facilitate external contact and to minimize oxidation of the indium during subsequent heating operations. The Silver Print overlay gives some difficulty after a period of time because it tends to lift up from the indium after several heating cycles. This results in a higher resistance of the finished cell. A suitable substitute for the Silver Print has not yet been found. A heavy evaporated silver, or other metal, overlay is partially successful but is inconvenient and is difficult to obtain in the desired thickness. Some attempts have been made to solder a wire lead directly to a thick electroplated indium electrode. This technique has been partially successful but only with very low melting (approx. 120°C) solders, which are not suitable for higher temperature operation.

In an attempt to secure a transparent collector electrode, thin evaporated films were studied. These were all much too high in electrical resistance to be considered. A silver layer 100 Å thick gives light transmission of only 50% and is still much too high in resistance.

A study of the method of forming a transparent layer described in U.S. Patent 2,694,761 (M.S. Tarnapol, Nov. 16, 1954) was made using $InCl_3$ on a glass substrate. We were unable to obtain films as low in resistance as those claimed. Resistances were much too high to be considered for CdS solar batteries.

Satisfactory results were obtained using a small indium spot on one corner of a single crystal, or using a narrow single or double stripe across the face of a polycrystalline plate. The resistance of the CdS compositions finally used was sufficiently low that contacting a single crystal at any point on one face gave adequate electric contact to the whole crystal. The stripes were needed for polycrystalline plates because occasional random cracks, or high resistance boundaries between adjacent grains, were encountered.

BARRIER ELECTRODE

Much of the crystal finishing work has centered on the formation of the barrier electrode. At the start, as was done at WADC, this electrode was electroplated from a saturated solution of $CuSO_4$ with a small amount of NH_4OH. It was then dried, heated, and contacted with Silver Print. It was found that the conditions of plating were very important to the results obtained. It developed that a dark brown coating, obtained at a current density of approx. 3 amps/cm^2 for about 2 seconds, gave best results. When the plating current density was decreased the coating

became reddish in color, and the finished crystal output was less. When the plating current was increased the color of the coating became purplish, and the power output of the finished cell also dropped off. It was thought that the coating obtained at optimum plating conditions must be mainly cuprous oxide, or at least a mixture of cuprous and cupric oxides. Late in the contract period x-ray diffraction equipment became available and an analysis of this material showed the deposit to be elemental copper and cuprous oxide with no cupric oxide present.

Varying the pH of the $CuSO_4$ plating solution (by adding HCl for pH's below 3.6, or by adding NH_4OH for higher pH's) had a tremendous effect on photovoltaic power output. A change in the plating solution occurs at a pH of about 5, with a copper salt being precipitated. Crystal voltage and power output dropped to zero when the barrier electrode was plated from the pH 5 solution. Maximum photovoltaic effect was obtained from solutions of pH 2 and 8.

Changing the concentration of the $CuSO_4$ in solution did not seem to affect results appreciably. Saturated solutions were used because of the ease of maintaining them.

Comparable crystal outputs were obtained with a very low pH $Cu(NO_3)_2$ solution. This solution was made up as follows:

30 gms	$Cu(NO_3)_2 \cdot 2H_2O$
100 cc	Conc HNO_3
500 cc	H_2O

The advantage of this plating bath was that plating conditions were comparatively non-critical and similar results were obtained over a wide range of plating currents and times. The best coating from this method

was usually dark grayish in appearance. One disadvantage of this bath was that it had to be changed every few days as its effectiveness dropped off with time. Presumably, copper went into solution from the anode, thus effectively changing the composition of the solution.

Several other types of copper plating baths were tried. A copper cyanide bath gave good metallic copper coatings, but no appreciable photo-voltaic outputs. A $CuCl + HCl$ bath gave crystals with reasonable outputs, but showed no particular advantage over the $Cu(NO_3)_2$ bath.

Other metals tried as a barrier electrode material included silver and nickel. These gave some photovoltaic effect, but nowhere near as much as obtained from the copper baths.

Much work was done trying to evaporate the barrier electrode. An evaporated barrier electrode would have advantages over the electroplated one since crystal area and resistance would be eliminated as variables in the electroding process. Initial attempts yielded reasonable open circuit voltages, as high as 0.44 volts, but at high resistances so that the power outputs were negligible. Different materials were evaporated including elemental copper, cuprous oxide, cuprous-cupric oxide mixtures, selenium sulfide, nickel oxide, and the material electroplated from the saturated $CuSO_4$ solution. Most of these gave crystals with some open circuit voltage, but none had appreciable power output. This evaporation process was not as easy to control as had been anticipated since heating the above materials in a vacuum caused indeterminate changes in the materials themselves prior to the actual evaporation. The oxides tended to reduce, so that it was difficult to determine just what material had been deposited on the crystal. In no case did a crystal with an evaporated barrier electrode

give a photovoltaic power output within an order of magnitude of the electroplated crystals. Hence, this effort was not pursued further.

In order to determine whether it was the material deposited on the crystal, or some characteristic of the electroplating process itself, which was important in securing a low-resistance photovoltaic cell, the following experiment was performed. A crystal with a newly-plated barrier electrode was air dried and placed against the freshly-ground and polished surface of a second crystal so that the electrode was physically against one surface of both crystals. The two crystals were heated while clamped together in this fashion, then separated and Silver Print applied to both crystals. When tested, reasonable photovoltaic power was secured from both crystals. Thus, it appeared that the electroplating process itself might be unnecessary and that equivalent or even better results might conceivably be obtained if the proper material were merely applied to one face of the crystals prior to heating.

Along these lines, acetone slurries of various materials were prepared and transferred with a spatula or eyedropper to cleaned crystal surfaces. Enough slurry was transferred to leave a thick layer of the materials on the crystal as the acetone evaporated. The crystals were heated in the standard manner, the excess material wiped off, contact made with Silver Print, and the crystal tested. Table 3 lists the various materials tried in this fashion with the maximum open circuit voltages and short circuit currents obtained.

While appreciable voltages and currents were occasionally obtained, there seemed to be no clear trend to the proportions of materials used, and none of the cells so made could compare with the regular electroplated

TABLE 3.

Acetone Slurries Deposited on CdS Crystals

No.	Materials	Proportions	Max. O.C.V.	Max. Current
1	Cu_2S	100%	.020 v	.0008 ma
2	CuS, Cu_2S	50-50	.020	.0003
3	CuO	100%	.020	.04
4	CuO, Cu_2O	80-20	.120	.04
5	"	70-30	.120	.25
6	"	60-40	.120	.40
7	"	50-50	.100	.40
8	"	40-60	.130	.18
9	"	20-80	.020	.06
10	Cu_2O	100%	.200	1.0
11	"	"	.280	.03

cells. Variations of the above techniques were tried, including mixtures of the various ingredients in vinyl resin, water slurries, and dry pressing the ingredients against cleaned crystal surfaces. None of these variations yielded significant results. Heating CdS crystals with various materials against one face was carried about as far as practical on an exploratory basis. The method still seems attractive, but further efforts along these lines should be guided by theoretical considerations of the proper materials to be used and the techniques of application.

At first the barrier was formed, after the barrier electrode had been plated, by heating on a hot plate at approx. 300-400°C. This process was difficult to control as the time of heating was so short. When crystals were potted in epoxy resin, the high temperature decomposed the plastic. It was found that equivalent results were obtained by heating in an oven at 110°C for 1 to 2 hours, without damaging the plastic. This method was effective in producing crystals of approx. 0.5 volts open circuit and power outputs in the order of 20 mw/cm^2 of barrier surface (under high levels of light intensity). After several months of using this process, however, it was found that longer and longer times of treating the crystals in the 110°C oven were necessary in order to bring them up to voltage. (Finally, these times were in excess of one week.) As a result, higher temperatures were evaluated[6] for the barrier formation. It was found that heating on the top of a temperature-controlled hotplate for 1 to 2 minutes was sufficient to form the barrier. A temperature of 300 to 350°C appeared to give best results. This method was used exclusively for the rest of the contract period. It is not understood why, after several months of satisfactory barrier formation at low temperatures, much higher temperatures

were necessary. One possibility is that a compositional change in the CdS crystals themselves slowed down the rate of diffusion of copper ions into the crystal lattice.

Three possible interpretations of the function of the heating process were suggested. Heating might be driving off residual moisture, oxidizing the copper-copper oxide layer, diffusing copper ions into the crystal a short distance, or a combination of these. In order to determine whether the heating process might be merely removing water from the barrier electrode, an attempt was made to form the barrier by drying an electroplated crystal in vacuum. This was only partially successful. Some voltage and power output was usually obtained, but subsequent heating always brought about an improvement. Heating a plated crystal in vacuum was not successful in forming a good barrier, hence it appeared that air is necessary along with the heating. Heating plated crystals in the presence of a strong oxidant (30% H_2O_2) did not appear to accelerate barrier formation, however. An attempt was made to form the barrier by diffusing copper into indium-doped CdS. An outside layer of the n-type CdS was converted to p-type, but the barriers so formed had poor photovoltaic properties.

The above described experiments were preliminary and do not permit definite conclusions as to the nature of the barrier. However, the experience to date suggests the following probable mechanism. Electroplating places a partially oxidized layer of copper in intimate contact with the face of the CdS crystal. This layer is finely sub-divided and heating probably changes more of the copper to cuprous oxide. However, heating may also do one of the following: it may cause the diffusion of cuprous ions into the crystal and form a p-type layer of CdS at the surface of the crystal;

or it may make a cuprous oxide film at the surface of the crystal p-type thus giving a p-n junction with the n-type CdS. Further work is necessary to resolve this uncertainty, but was not practical during this contract because of the limited time available and the limited scope of the contract.

Some work has been done to improve the electrical contact to the barrier side of the crystal. Normally, after the barrier electrode is applied, it is air (or vacuum) dried, covered with Silver Print, and then heated to establish the barrier. The Silver Print is applied prior to heating since contact to the barrier electrode is necessary to determine when optimum power output has been obtained. This heating frequently causes the electrode, or the Silver Print layer, to lift and thus increase the contact resistance. A method to get around this difficulty was developed. After heating, the material on the barrier face was removed by rubbing with an acetone-wet paper tissue, or by polishing with very fine alumina grit on a wet felt lap. The apparently bare crystal face was then re-dried and re-covered with fresh Silver Print. It was found that in nearly all cases the output of the cell was improved. The improvement resulted from a lowered resistance and, occasionally, from a higher open circuit voltage. Even better results were obtained when metallic silver was evaporated on the exposed crystal surface in place of the Silver Print.

TESTING

The equipment used for testing finished cells and batteries was arranged as described below. A spring clip with the two jaws insulated from each other was used to hold the crystals or batteries in position under the light and to make contact to the electrodes. Wires were soldered

to each jaw of the spring clip and connected, through a reversing

switch, to a Keithley Model 210 electrometer equipped with a decade

shunt, a Simpson Model 269 multiscale volt-ohm-milliammeter, and an

L. & N. resistance box. By this means, cells or batteries could be

tested for voltage and current outputs into various resistive loads.

A GE radiation meter, Model 8DW60Y2, calibrated in heat values from

0 to 2 gm-cal/cm^2/min, was used to check the level of illumination.

Initially, a 500-watt TDC "Stream Liner 500" slide projector

was used as a light source for checking the photo sensitivity of single

cadmium sulfide crystals. This was satisfactory for securing high levels

of illumination over small areas. The level of illumination and the

spectral distribution of this source were not determined. In order to

have a light source with a spectral energy distribution more closely

resembling that of the sun, a Westinghouse 1000-watt xenon short arc lamp

was secured. This illuminated larger areas but suffered the drawback of

having a very uneven level of illumination over the larger areas. It was

found that a more convenient source of illumination for larger areas

(such as required for the completed batteries), at levels of illumination

in the range of 1 to 2 on the GE radiation meter, was obtained by using

a standard reflector type photoflood or photospot lamp, although the

spectral energy distribution does not match that of sunlight as well as

the xenon short arc lamp.

There have been a number of indications that conversion efficiency

increases as the level of illumination is increased. Figure 5 shows the

variation in output of a CdS single crystal measured over the range of

illumination of 0 to 2.0 on the GE radiation meter. The non-linearity

LIGHT INTENSITY   -   GM CAL/CM²/MIN
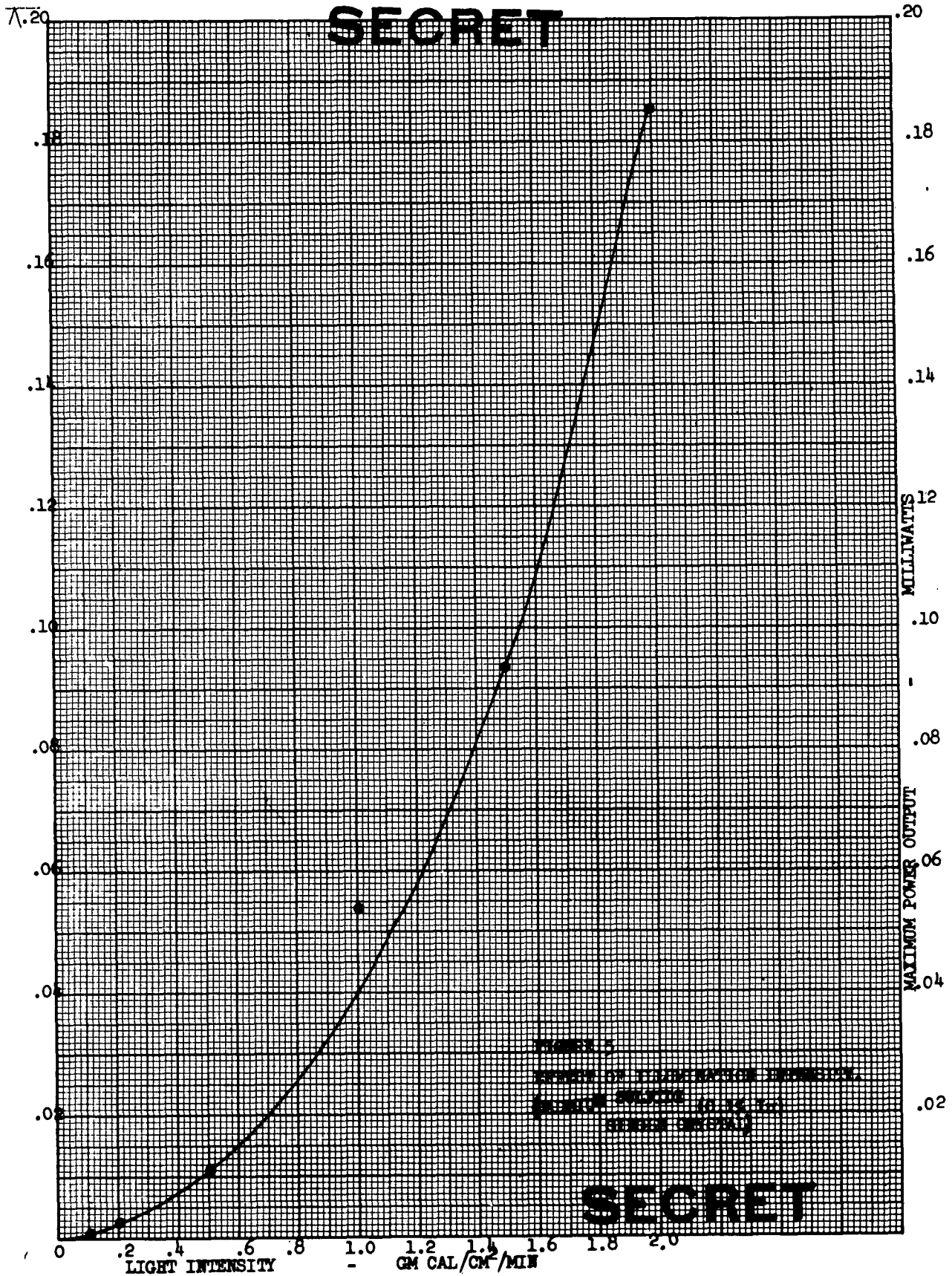
of output with illumination is immediately apparent. Lack of suitable means of measuring higher levels of illumination has prevented the extension of this curve. It may be that the increased conversion efficiency at higher illumination is due to a photoconductive effect. Further work along these lines is indicated.

Lacking a good reproducible method of barrier formation, it was difficult to evaluate various growth runs, especially when only a few usable crystals might be available from some lots. Hence, in order to determine and compare the semi-conducting properties of the CdS crystals themselves an apparatus was constructed to make Hall measurements. A modified Cinaudagraph, Type 6.3A485, permanent magnet of approx. 5,000 gauss field strength was used. Figure 6 shows schematically the arrangement of this equipment. Crystals to be measured for Hall coefficient were cut to approx. 1 cm x 0.2 cm x 0.08 cm in size, and 6 indium contacts were plated for the appropriate connections. Crystal conductivity was calculated from the current and potentiometer readings and the measured dimensions of the crystals. Hall coefficient and mobility were calculated from the Hall voltage taken at fixed values of current flow and magnetic field strength at room temperature.

Table 4 lists the Hall measurements of several cadmium sulfide single crystals at three different levels of indium doping. The measurements show that in general the concentration of carriers decreases with decreasing amounts of added impurities, but that the mobility does not apparently change. The correlation between the concentration of charge carriers in the grown crystals and the amount of In_2S_3 added to the pre-growth mixture is not good. This may be due to imperfections in the
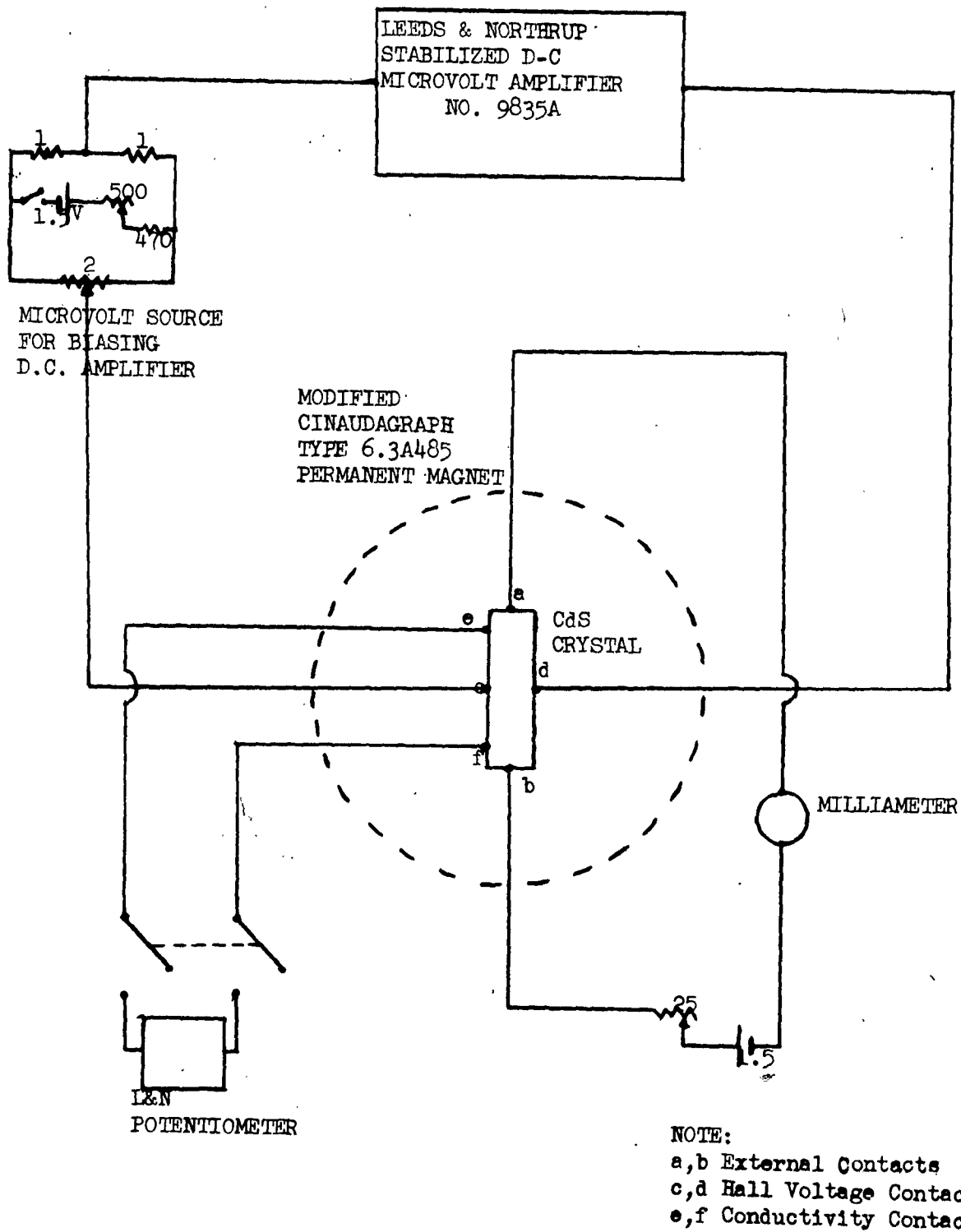
LEEDS & NORTHRUP
STABILIZED D-C
MICROVOLT AMPLIFIER
NO. 9835A

500

470

1.5V

1

1

2

MICROVOLT SOURCE
FOR BIASING
D.C. AMPLIFIER

MODIFIED
CINAUDAGRAPH
TYPE 6.3A485
PERMANENT MAGNET

CdS
CRYSTAL

e

a

d

c

f

b

MILLIAMETER

25

1.5

L&N
POTENTIOMETER

NOTE:
a,b External Contacts
c,d Hall Voltage Contacts
e,f Conductivity Contacts

FIGURE 6. Hall Testing Apparatus

TABLE 4.

Hall Measurements on CdS Single Crystals at Room Temperature

CdS Lot	In$_2$S$_3$ Doped %	Hall Constant	Carrier Concentration electrons/cm^3	Conductivity (ohm-cm)$^{-1}$	Mobility cm^2/volt-sec
67	0.10	-0.916	7.6 x 10^{18}	225	190
77	0.10	-1.4	4.9 "	92	120
108	0.05	-0.89	7.9 "	65	50
110	0.05	-1.36	5.2 "	162	200
131	0.05	-0.73	9.6 "	457	300
101	0.01	-5.8	1.2 "	34	180
99	0.01	-4.5	1.5 "	51	200

crystal samples, or to difficulties in contacting these small crystals.
Additional data over a wider range of impurity addition are required.

Since higher conversion efficiencies were being obtained at WADC,
spectral response curves on several CdS crystals were obtained to make
sure that the different CdS material used for this work was not giving
a radically different photovoltaic response. Figure 7 is a typical
curve showing the variation in photovoltaic response with wavelength.
A Beckman DU spectrophotometer was used as a light source with an
L. & N. DC microvoltmeter as an indicator. The results were in good
agreement with data published by Reynolds of WADC[1].

A series of CdS optical transmission curves are given in Figure 8
in which the effect of various impurity additions on the absorption cut-
off is shown. These were run on a GE recording spectrophotometer and,
while the indicated optical transmissions are low due to scattering of
light by fractures, the positions of the cut-off as shown are accurate.
The horizontal portion at the left of each curve is its zero transmission.
(The curves, when they were re-drawn, were displaced for clarity.) The
transmissions were run through 1-1/2 mm thick pieces of CdS crystal doped
as indicated. Chloride doping gave the lowest cut-off with different
concentrations shifting the cut-off only slightly. ZnS and In_2S_3 together
gave the highest value with greater concentrations of ZnS showing an
appreciable shift. It had been hoped that a substantial lowering of the
absorption cut-off could be obtained and that this would result in a higher
conversion efficiency.

Figure 9 presents the results of a test made to evaluate the effect
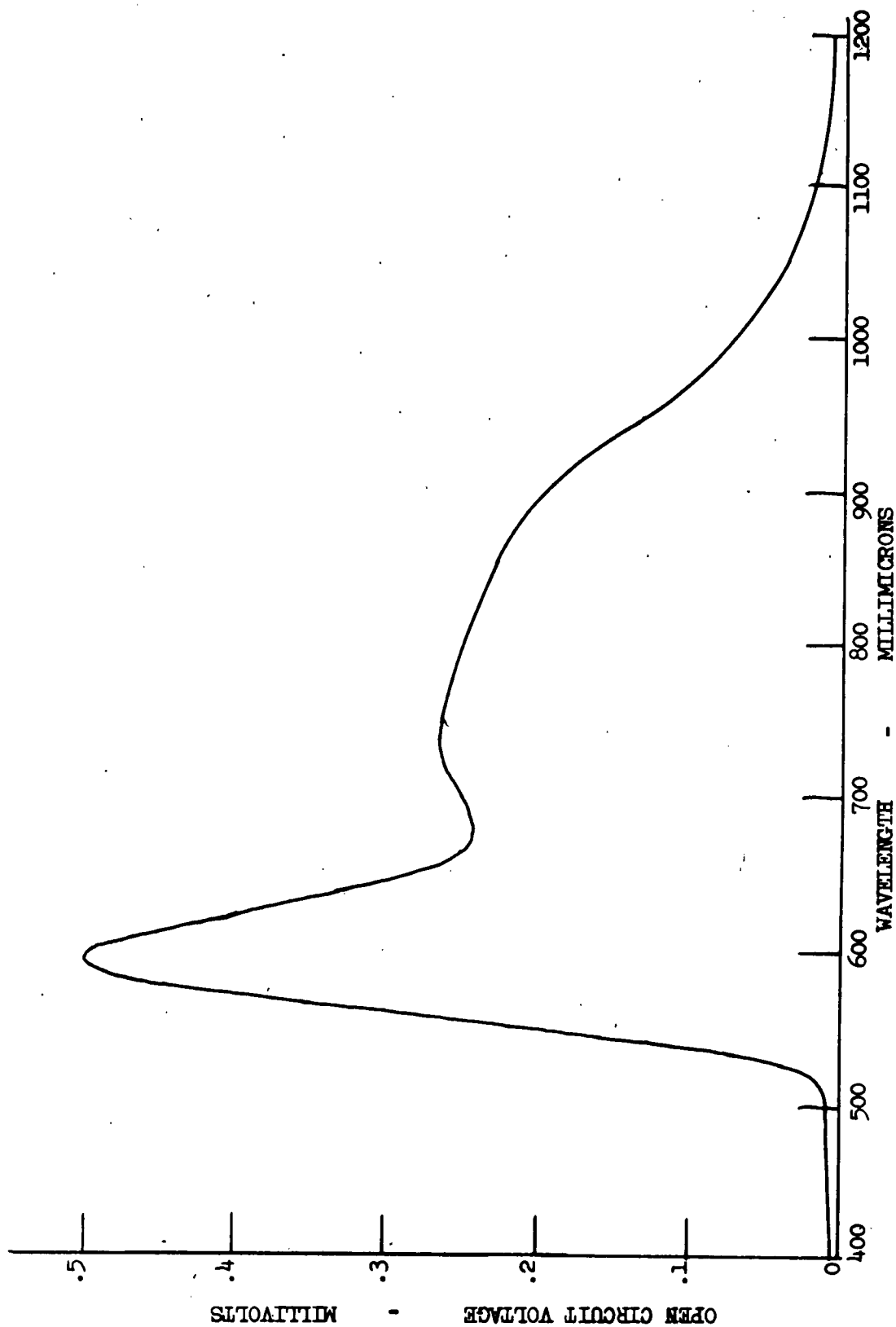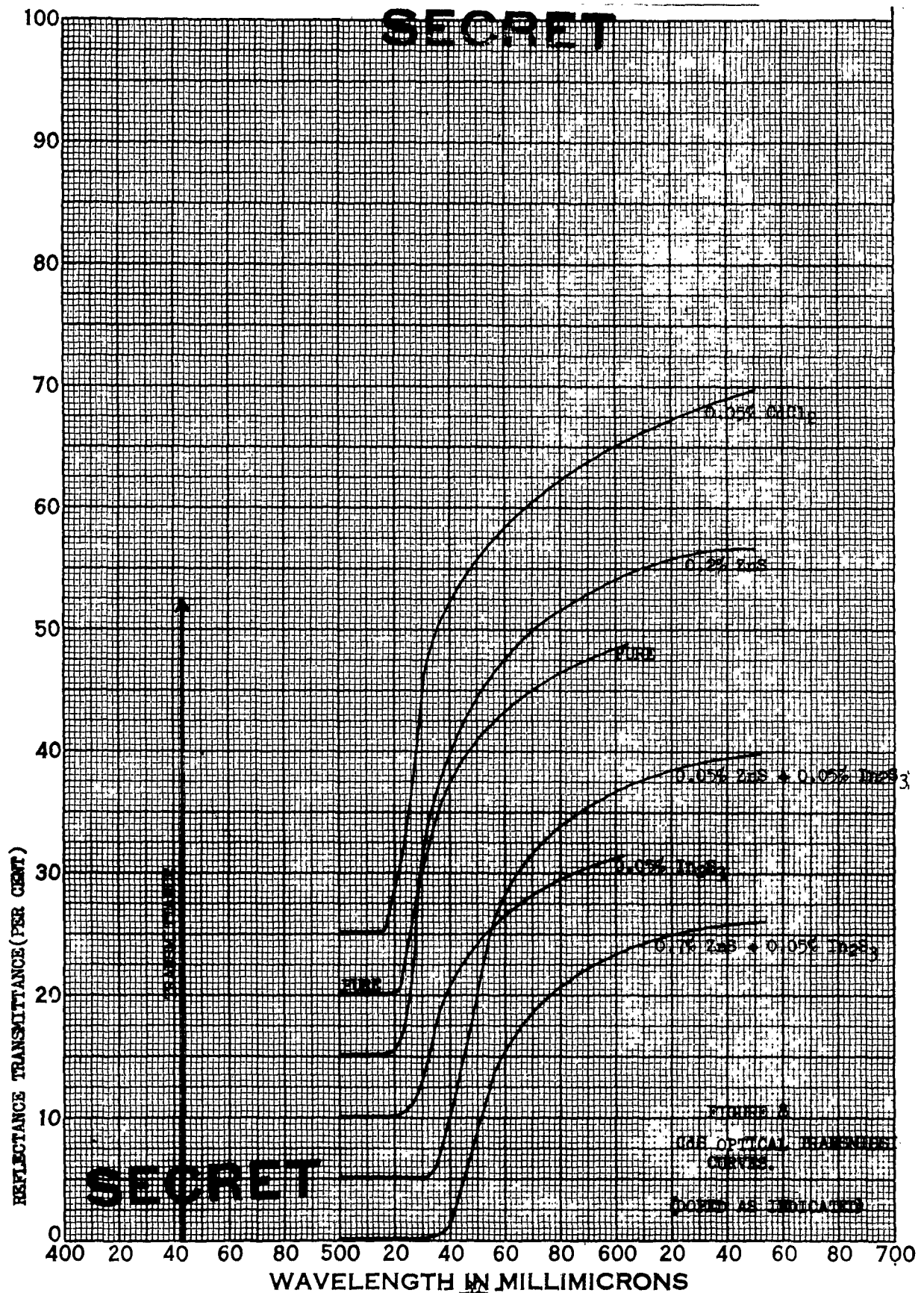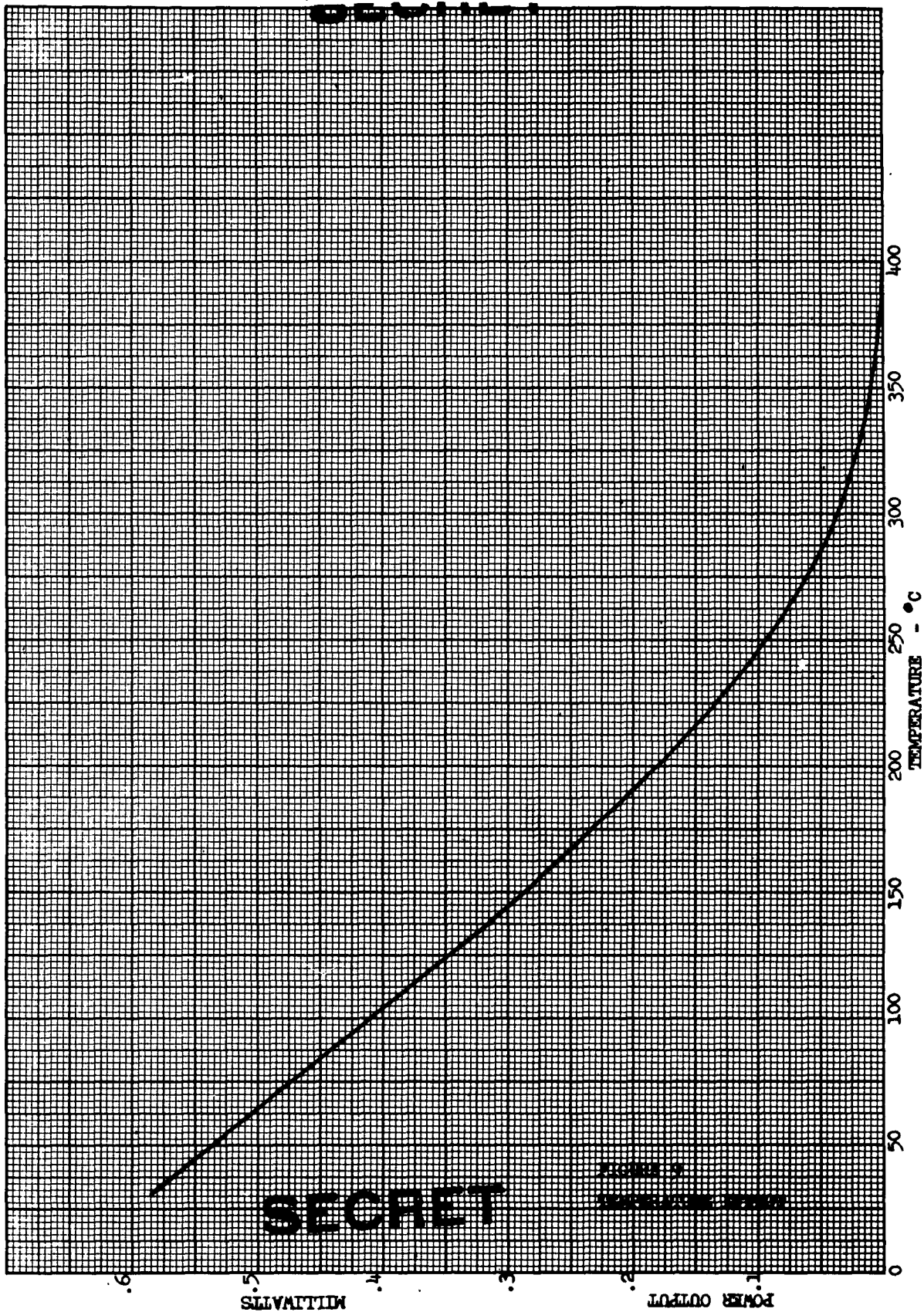of temperature on power output. It is seen that the output drops off with

FIGURE 7
CdS(In) SPECTRAL RESPONSE CURVE

FIGURE 8.
CdS OPTICAL TRANSMISSION
CURVES
DOPED AS INDICATED

X-axis: WAVELENGTH IN MILLIMICRONS
Y-axis: REFLECTANCE TRANSMITTANCE (PER CENT)

Curves labeled: 0.05% CdCl₂, 0.2% ZnS, PURE, 0.05% ZnS + 0.05% In₂S₃, 0.05% In₂S₃, 0.1% ZnS + 0.05% In₂S₃, PURE

increasing temperature. At 150°C, the output is about half the room temperature value. Some power output is obtained even at temperatures of 350 to 400°C.

It has been noticed that the photovoltaic output of finished cells tends to decrease with time. The fall-off is normally slow and extremely irregular. This degradation was assumed to be due to moisture adsorption. Coating the barrier face of cells with "Krylon" plastic slows down the effect. Encapsulating the crystals in epoxy resin appears to be much more effective, but still some fall-off has been experienced. A few experiments with moisture exposure were made in order to evaluate this effect more completely. In one experiment, unprotected crystals exposed to 100% humidity for about one week showed nearly complete loss of voltage and power output. However, a short re-heating of these crystals was sufficient to restore the original output. In other experiments, individual crystals were exposed to less than 100% humidity for longer periods of time. The results were erratic but eventually all crystals so exposed showed a definite drop-off in output. Again, complete recovery was obtained on re-heating the crystals.

The highest conversion efficiency recorded during this contract was 1.0% on a single crystal of 0.033% In_2S_3-doped CdS tested in direct sunlight. The highest open circuit voltage was 0.525 volts on 0.2% In_2S_3-doped CdS in a focused 750-watt projector lamp beam. These data are not entirely comparable since crystals were measured under different illumination sources and intensities. During the latter part of the contract conversion efficiencies in the range of 0.3 to 0.5%, and open circuit voltages in the range of 0.4 to 0.5 volts, were the best that could be obtained on 0.02% In_2S_3-doped polycrystalline plates at 2.0 light intensity.

BATTERIES

An interim technique was developed for assembling CdS cells into
a battery. Batteries so constructed are satisfactory for use up to
approx. 120°C. The method consists of cementing the cells against a
prepared etched circuit and encapsulating in epoxy resin. A copper
clad, epoxy resin filled, glass base laminate is used as the base material.
The individual crystals (or polycrystalline plates) are prepared by
removing the Silver Print from the barrier electrode with an acetone-wet
tissue and evaporating approx. 100 Å of silver metal onto the barrier
surface. The crystals are then fastened to the prepared laminate using
epoxy resin as the cement. Electrical contact between the barrier elec-
trode and the copper cladding is established by sprinkling coarse (about
60/80 mesh) silver particles between the crystal and the copper so that
these silver particles bridge the epoxy cement layer. The assembly is
held under moderate pressure until the resin is cured.

Terminals are inserted to make contact to the copper cladding
through the back of the laminate. The terminals are soldered to the copper
laminate, and epoxy resin is filled in around the crystals to bring the
plastic level up to the indium electroded faces of the crystals. Negative
terminals are inserted in holes drilled through the entire assembly from
the back. Connection can be made by printing a conducting path with
Silver Print, by soldering a wire lead, or by cementing a silver foil
strip between the terminals and the corresponding indium electrodes.

On the last six batteries constructed, prior to inserting the
negative terminals, the top surface of the assembly was ground flat, so
that the indium electrodes were removed and the surfaces of all cells

were level. They were re-polished and the indium electrodes re-plated.
Electrical connections for re-plating were made through the crystals
themselves, with no deleterious effects to the barriers being detected.
The negative terminals were then inserted and connection made between
the terminals and the newly plated indium electrodes.

The whole assembly was then encapsulated in clear epoxy resin
and ground and polished so that only a thin layer, approx. 1 mm thick,
of plastic was left above the crystals. The cells were then connected
in series and/or parallel, as desired, by wiring between the terminals
projecting from the back of the battery.

Nine batteries were manufactured during the course of the present
contract. Battery "B-1" was constructed of 13 large sized single crystals
connected in a series-parallel arrangement, and encapsulated in a block
of clear epoxy resin. This battery, under the xenon arc lamp, gave 0.65
volts open circuit and 4.0 milliwatts of power into a 40 ohm load. The
output from this battery was appreciably less than the calculated sum of
the individual crystal outputs, and continued to drop off with age.

Battery "B-2" was assembled from 40 medium sized single crystals,
arranged in jigsaw-puzzle fashion, cemented down onto four 3/4-in square
copper sheets which were connected in series. These squares were laminated
to a thin sheet of phenolic resin and then encapsulated in clear epoxy resin.
Figure 10 shows a photograph of this battery. The power output curves at
different levels of illumination are presented in Figure 11. After approx.
4-1/2 months of age, the output of Battery "B-2" had dropped to less than
half of its original value, as seen by the dashed curve in Figure 11. The
individual crystals going into "B-2" were coated with a heavy layer of
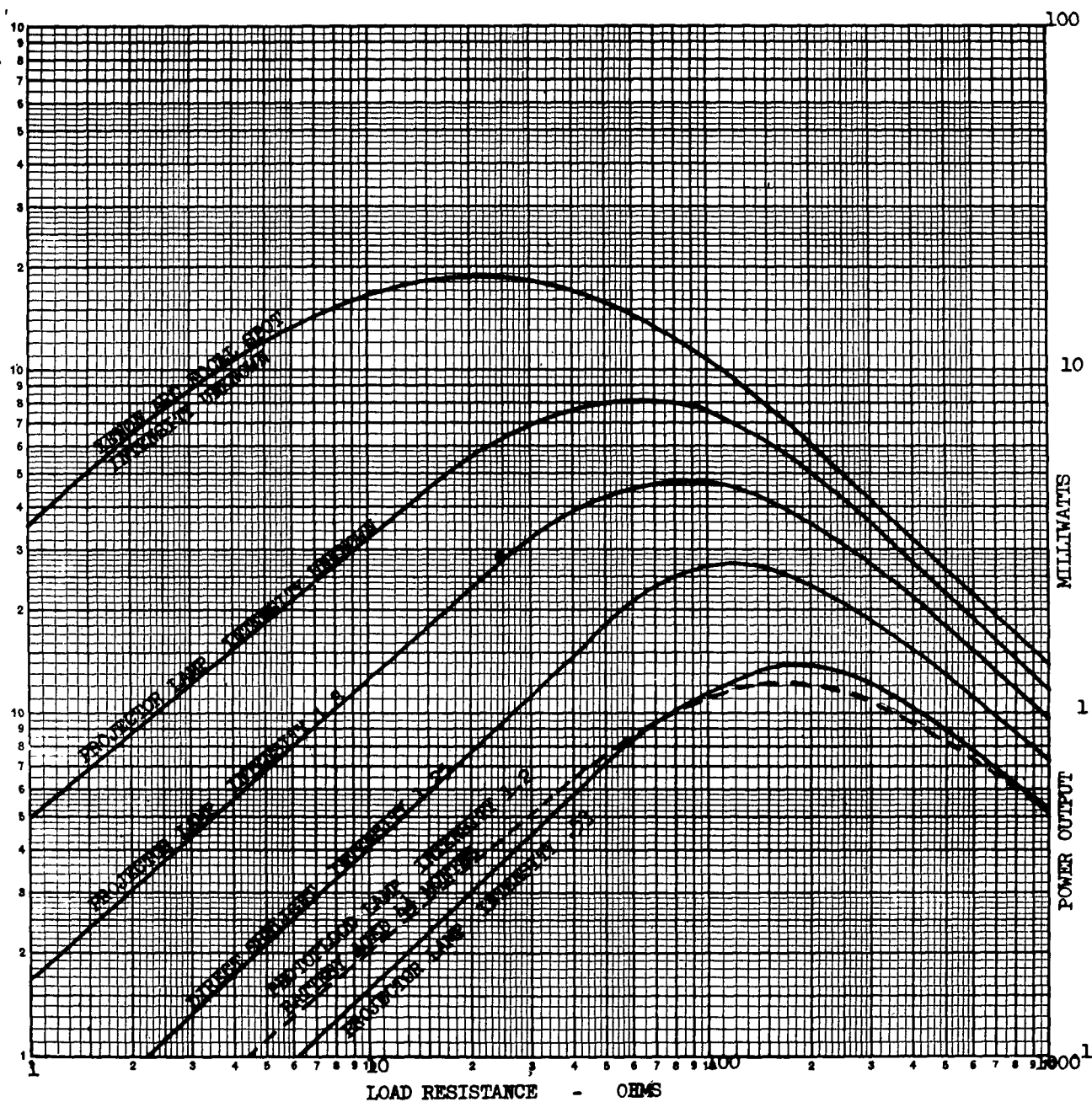
Front View
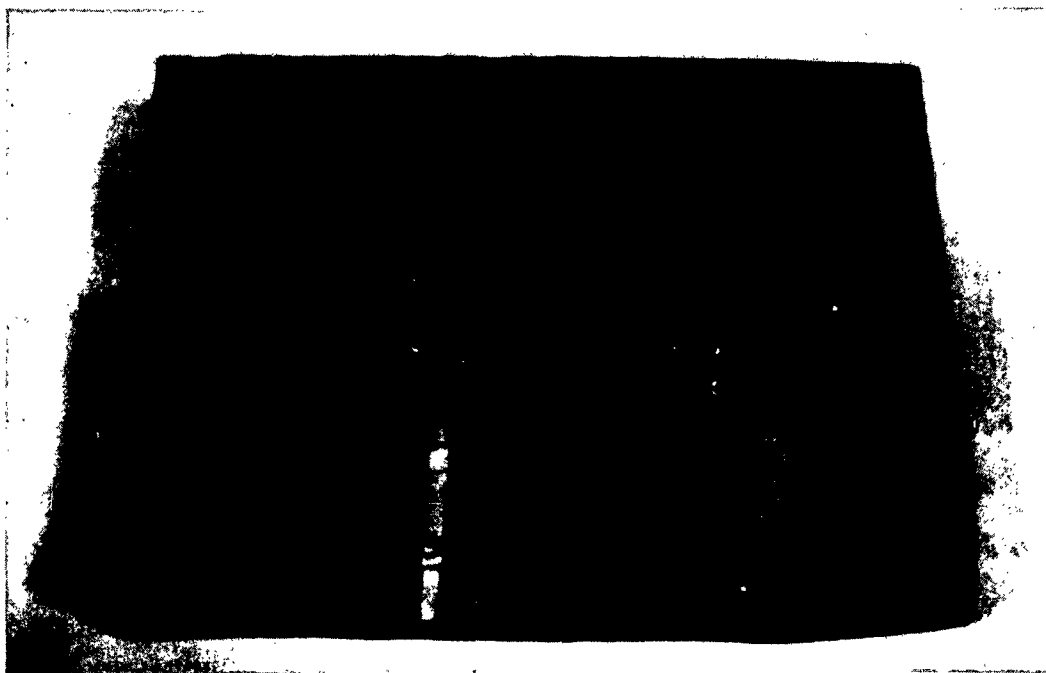
Back View

Figure 10. - Battery B-2

Figure 11. Power Output Curves - Battery B-2

Silver Print over their barrier electrode surfaces prior to cementing to the copper sheets. This Silver Print layer may have lifted, thus accounting for the drop-off in output with age. On subsequent batteries this Silver Print layer was eliminated.

Battery "B-3" was made from eight polycrystalline plates approx. 20 mm in diameter. The plates were cemented to individual discs of copper clad laminate and these, in turn, were cemented to a backboard of thin phenolic plastic, and the whole encapsulated in epoxy resin. A picture of this battery appears in Figure 12. Battery "B-3" was constructed hurriedly for the exhibition at the recent Solar Energy Symposium at Phoenix, Arizona, and tested only briefly before delivery. With the cells connected with four parallel pairs in series, the battery initially delivered approx. 5 milliwatts into a 25 ohm load and had an open circuit voltage of approx. 0.8 volts at 1.2 xenon arc illumination (equivalent to bright noonday sunlight).

Batteries "B-4" to "B-9", inclusive, were made according to the interim techniques described at the beginning of this section. Batteries "B-4" to "B-8" consisted of eight polycrystalline plates 20 mm in diameter, and looked similar in appearance to Battery "B-3" as shown in Figure 12, while "B-9" consisted of 4 such plates 40 mm in diameter. The highest conversion efficiency was secured from Battery "B-7". This yielded 15 mw at a light intensity of 2.0 on the GE radiation meter. For a crystal area of 25 cm^2 this gives an efficiency of 0.36%. Under a light intensity of 1.2, the maximum power output was 7.0 mw for an efficiency of 0.28%. Figure 13 gives the power output curves for "B-7" at 1.2 and 2.0 illumination.
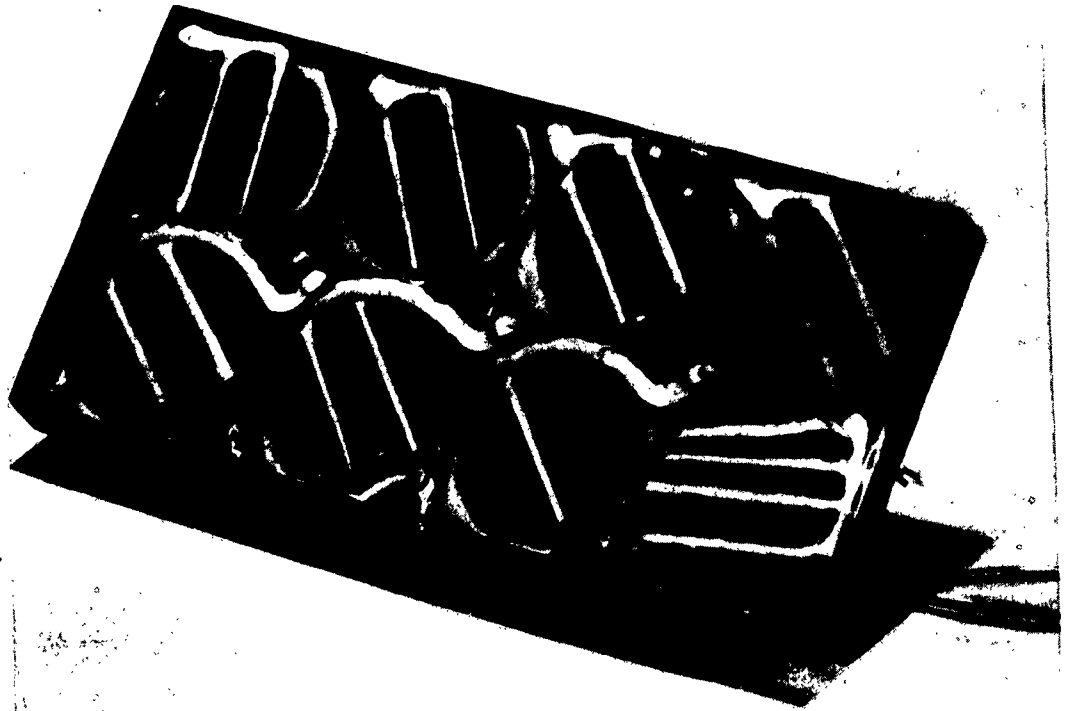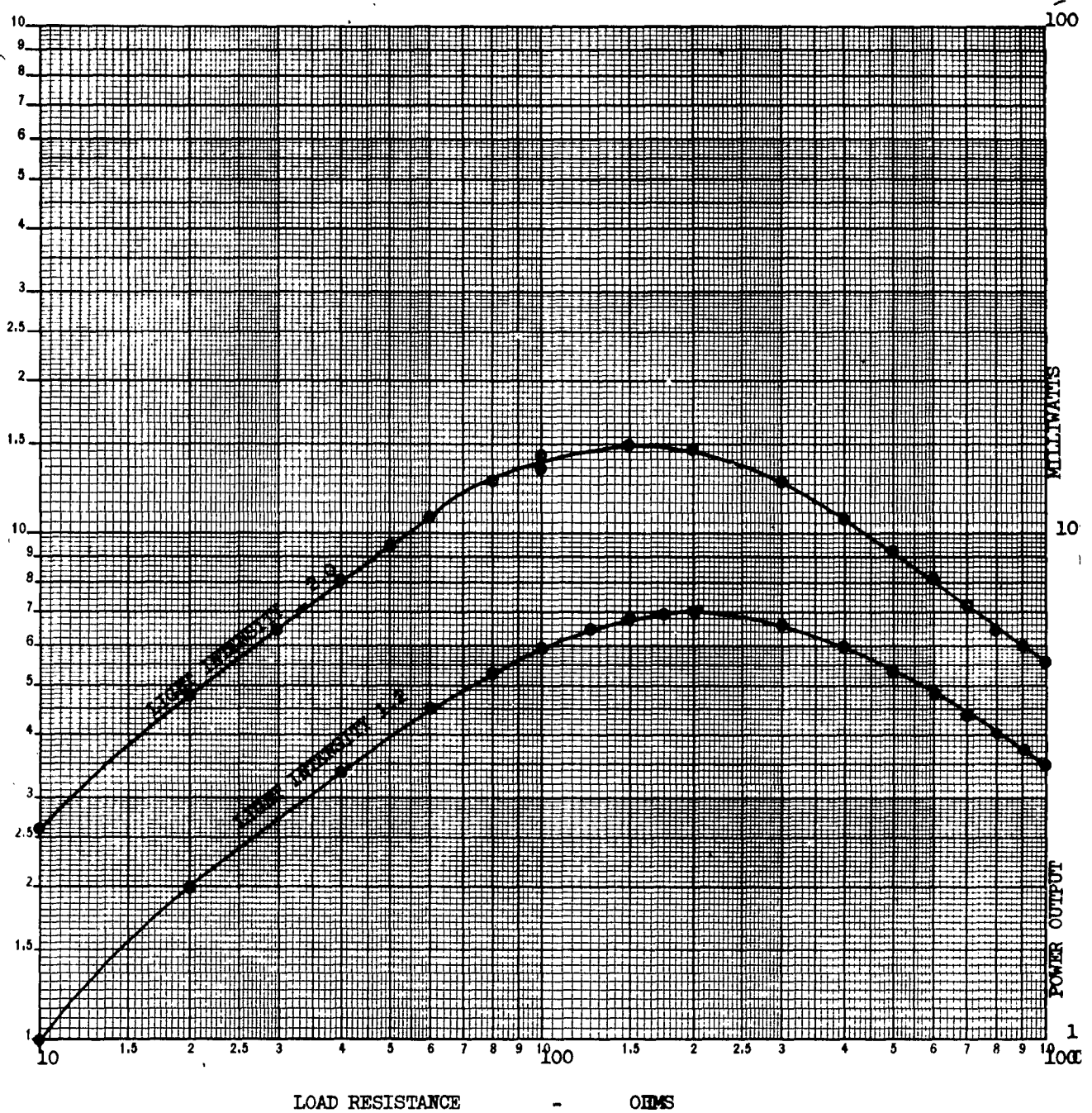
Front View
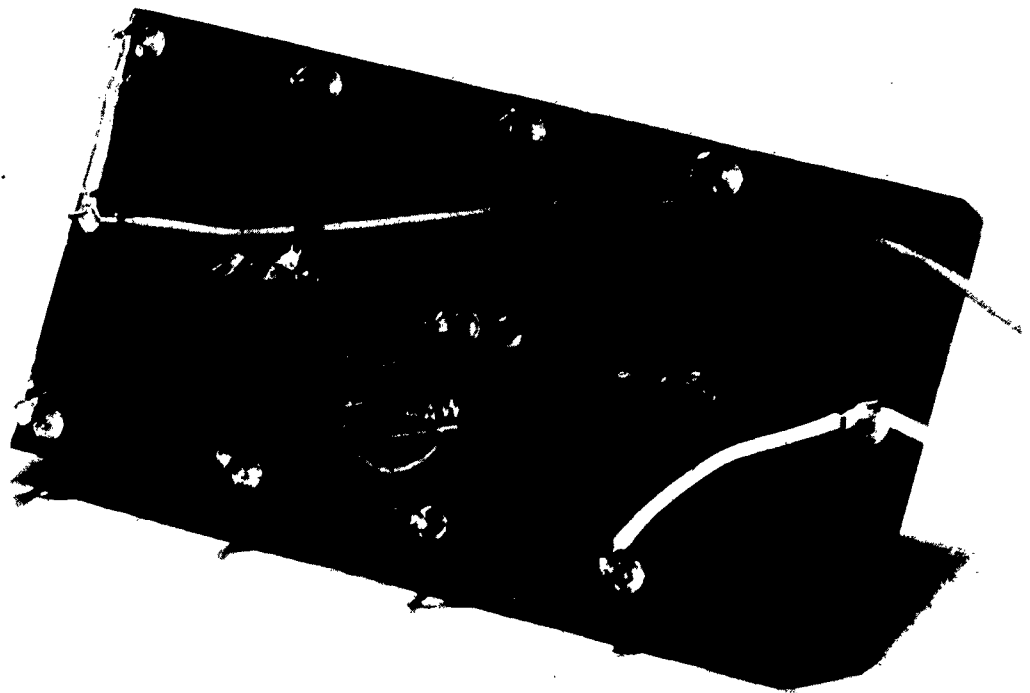
Back View

Figure 12. - Battery B-3

Figure 13. Power Output Curves - Battery B-3

Batteries "B-4" to "B-9", inclusive, were connected in series and their output under an uneven illumination of approx. 2.0 average was fed to a small electric motor. Under these conditions they delivered initially over 100 milliwatts of power at 2.8 volts. On open circuit they gave 6.5 volts. These outputs dropped as the batteries heated up under the high light level.

SECRET

SUMMARY

CdS materials from various sources were evaluated for single crystal growth runs. GE Luminescent Grade CdS, doped with In_2S_3, was used for most of the work on this contract. Single crystals of CdS were grown by the method of Reynolds and Czyzak, and a technique for growing poly-crystalline plates was developed. Attempts to grow crystals by the vapor reaction method and from fused salt mixtures were unsuccessful.

A number of materials were tried for impurity doping of the CdS including ZnS, In_2S_3, $In_2(SO_4)_3$, Ag_2S, CuS, CdO, Cd, $CdCl_2$, NaCl and some mixtures of these. Best results seemed to be obtained with In_2S_3 added to the GE Luminescent Grade CdS in the proportion of about 0.02% by weight.

Single crystals were prepared for electroding by potting in epoxy resin, cutting to rough thickness, and grinding and polishing to final thickness. Optimum crystal thickness seems to be in the neighborhood of 2 mm. Polycrystalline plates did not usually require potting in plastic prior to grinding to thickness. Cleaning and etching of the crystals prior to electroplating was occasionally beneficial.

Among materials tried as a collector electrode were indium, cadmium, and gallium. Collector electrodes were both electroplated and evaporated. Best results were obtained from electroplated indium protected with an overlay of Silver Print. Small indium spots, or indium stripes, covering less than 10% of the illuminated face of the crystal, gave excellent ohmic contacts to n-type CdS crystals.

Much work has been done with different types of barrier electrodes, but the nature of the barrier itself is still uncertain. Best results to date have been obtained with a barrier electrode electroplated from either

SECRET

a saturated $CuSO_4$ solution of 8 pH or from a low pH $Cu(NO_3)_2$ solution and heat treated at 350°C for about 2 minutes. Evaporated barrier electrodes and attempts to diffuse the barrier have not been successful. Generally, the contact to an established barrier can be improved by removing the excess electroplated material and re-applying silver or Silver Print.

Spectral response curves for CdS(In) corroborate previously published data. Optical transmission curves for CdS show only slight shifts in the cut-off wave length for the various dopings tried. Energy conversion efficiency increases as the light intensity is increased, but falls off as temperature is increased. At 150°C the power output drops to about half the room temperature value. Some output is obtained up to 400°C. The best efficiency obtained during the contract was 1.0% on a single crystal in direct sunlight.

A technique for assembling crystals and polycrystalline plates into batteries was developed. Such batteries can be operated only up to temperatures of about 120°C. Nine batteries were assembled - two from single crystals and seven from polycrystalline plates. These delivered initially a total of approx. 36 millivatts of power in direct sunlight. This was less than initially anticipated due, mainly, to two unforeseen difficulties: the lack of success in growing large usable single crystals, and the inability to form good barriers. Additional information on the fundamental nature of the barrier is needed.

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